Acyl sulfonates $(CH_3)_2CHCOOSO_2CH_3$, $CH_3CH_2COOSO_2CH_3$, $CH_3CH_2COOSO_2C_6H_4CH_3$-*p*, and $CH_3COOSO_2CH_3$ were prepared according to the literature.[20] Diphenylacetyl methanesulfonate was prepared by the reaction of diphenylketene (1.05 g, 5.4 mmol) with methanesulfonic acid (0.35 mL, 5.4 mmol) in CCl_4 (3 mL) at room temperature: NMR (CCl_4) δ 3.0 (s, 3 H, SO_2CH_3), 5.0 (s, 1 H, =CHCO), 7.2 (s, 10 H, aromatic).

Raman Spectrum. The Raman spectrum of a mixture of acetic acid (3 mL, 52 mmol) and $ClSO_3H$ (1.3 mL, 25 mmol) after heating at 80 °C for 30 min showed two new peaks at 395 and 1050 cm^{-1} in addition to the peaks assigned to the components of the mixture. These two peaks were identical with those of *O*-monoacetyl sulfate.[16c]

Kinetics of Iodination of Dimethylketene and Bromination of Diphenylketene. The reaction of dimethylketene with iodine followed by hydrolysis and esterification with diazomethane gave methyl α-iodoisobutyrate, which was identified by GLC. The kinetics of iodination of dimethylketene were determined in a quartz UV cell themostated at 20 °C. The reaction was started by addition of a 1,2-dichloroethane solution (1 mL) of 3.6×10^{-3} M dimethylketene into a dichloroethane solution (2 mL) of 2.4×10^{-3} M iodine. The rate of the reaction was followed by measuring the UV absorbance of iodine at 500 nm (ϵ 910). The initial concentration of dimethylketene was determined iodometrically after addition of excess bromine to consume the ketene.

Bromination of diphenylketene in dichloroethane to give α-bromodiphenylacetyl bromide was done similarly in a quartz UV cell at 30 °C. The rate was followed by measuring the UV absorbances of diphenylketene and bromine. Since their absorbances overlapped at their absorption maxima at 405 nm, three wavelengths, 390, 405, and 420 nm, were used for the measurements of concentrations.

Kinetics of Reactions of Iodine and Bromine with Carboxylic Anhydride-Sulfuric Acid (Monoacyl Sulfates). Into a solution of iodine (1 g, 4 mmol) in propionic acid (30 mL) maintained at 80 °C was added 97% H_2SO_4 (1 mL, 18.8 mmol), and the reaction was started by addition of propionic anhydride (2 mL, 15.4 mmol). Aliquots were taken at appropriate time intervals, and the concentration of iodine was determined iodometrically.

Similarly, the bromination of monopropionyl sulfate was conducted with bromine (1.2 g, 7.8 mmol) at 60 °C. The rate measurements for the iodination and bromination of monoacetyl sulfate were conducted in acetic acid in the same way as above, where acetic anhydride (4 mL, 42.3 mmol) and H_2SO_4 (1 mL, 18.8 mmol, for iodination; 0.23 mL, 4.7 mmol, for bromination) were dissolved in acetic acid (25 mL).

Kinetics of Bromination of Diphenylacetyl Methanesulfonate. Diphenylacetyl methanesulfonate was prepared by the reaction of diphenylketene (3.3 g, 17 mmol) with methanesulfonic acid (1.1 mL, 17 mmol) in 1,2-dichloroethane (5 mL) at room temperature, and the solution was diluted to 10 mL with dichloroethane to prepare 1.7 M diphenylacetyl methanesulfonate. The solution (3 mL) was added to dichloroethane (30 mL) containing bromine (1.2 g, 7.5 mmol) at 60 °C. Aliquots were taken at appropriate time intervals to follow iodometrically the decrease in the concentration of bromine.

Iodination and Bromination of Acyl Sulfonates. Iodinations of isobutyryl, propionyl, and acetyl methanesulfonates and propionyl *p*-toluenesulfonate were attempted in 1,2-dichloroethane (50 mL) containing iodine (2 g, 7.9 mmol) and the acyl sulfonate (20 mmol) at 80 °C for 5 h, but no reaction was observed.

Analogously, brominations of acyl sulfonates (20 mmol) were conducted in dichloroethane (50 mL) containing bromine (1.2 g, 7.5 mmol) at 60 °C. The consumptions of bromine after 3 h were 40% for propionyl methanesulfonate, 15% for propionyl *p*-toluenesulfonate, 50% for isobutyryl methanesulfonate, and 40% for acetyl methanesulfonate. These brominations gave the corresponding methyl α-bromocarboxylates on hydrolysis and esterification, identified by GLC comparison with authentic specimen.

Acknowledgment. We thank Daicel Chemical Industries Ltd. and Mitsubishi Chemical Industries Ltd. for their gifts of materials and also Mr. M. Inaishi for typing the manuscript.

Registry No. $CH_3CO_2SO_3H$, 2308-54-5; CH_3CO_2H, 64-19-7; $C_2H_5CO_2SO_3H$, 40268-66-4; $C_2H_5CO_2H$, 79-09-4; $(C_6H_5)_2C{=}C{=}O$, 525-06-4; $(C_6H_5)_2CHCO_2H$, 117-34-0; $(C_6H_5)_2CHCO_2SO_2CH_3$, 80583-49-9; propionyl methanesulfonate, 26926-30-7; propionyl *p*-toluenesulfonate, 26926-29-4; isobutyryl methanesulfonate, 26926-34-1; acetyl methanesulfonate, 5539-53-7; dimethylketene, 598-26-5.

---

[20] Karger, M. H.; Mazur, Y. *J. Org. Chem.* 1971, *36*, 528.

Substituent Parameter Analysis of the Carbon-13 Nuclear Magnetic Resonance Chemical Shifts of 4-Substituted *p*-Terphenyls[1]

Nancy K. Wilson* and Robert D. Zehr

U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711

Received September 14, 1981

The effects, $\Delta\delta$ values, of substituents at the 4-position of 1:1′,4′:1″-terphenyl on the ^{13}C NMR chemical shifts were measured. For the set of substituents R = NO_2, $COOCH_3$, CN, H, CH_3, I, Br, Cl, NH_2, and $N(CH_3)_2$, correlations between $\Delta\delta$ values and various inductive and resonance σ parameters were sought by using three models: a single-parameter relationship, $\Delta\delta = \rho\sigma$; a dual substituent parameter (DSP) relationship, $\Delta\delta = \rho_I\sigma_I + \rho_R\sigma_R$; a nonlinear dual substituent parameter (DSP-NLR) relationship, $\Delta\delta = \rho_I\sigma_I + \rho_R\sigma_R/(1 - \epsilon\sigma_R)$. No acceptable correlations were obtained for the ^{13}C shifts of C-3,5 and C-4. A single parameter, $\sigma_R{}^0$, was adequate at only two positions, C-2′,6′ and C-2″,6″. At positions C-1, C-2,6, C-3′,5′, C-1″, C-3″,5″, and C-4″ the DSP model and $\sigma_R{}^0$ were best. At para-type positions in the central ring (C-1′ and C-4′) the DSP-NLR model was best. The magnitude of the ratio $\lambda = \rho_R/\rho_I$ of mesomeric to inductive transmission of electronic substituent effects ranged from 0.535 to 4.58, indicating the importance of inductive electronic effects at nearly all positions in *p*-terphenyl, even at C-4″, the carbon farthest from the substituent, where λ = 1.70.

The nature of substituent effects on ^{13}C NMR spectra and the best choices of models to correlate them with classical measures of substituent effects on chemical reactivity such as the Hammett σ parameters have been of research interest for some time[2-13] and are the subjects of

---

[1] Presented in part at the 178th National Meeting of the American Chemical Society, Washington, DC, Sept 1979, and at the Southeast-Southwest Regional Meeting of the American Chemical Society, New Orleans, LA, Dec 1980.

[2] Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 1-20.

[3] Hehre, W. J.; Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 159-187.

[4] Nelson, G. L.; Williams, E. A. *Prog. Phys. Org. Chem.* **1976**, *17*, 229-342.

several papers in the recent literature.[14-22] We sought to answer two questions: which of the equations and parameters proposed in the literature are the best to describe terphenyl substituent effects, and what do the correlations between substituent parameters and substituent effects tell us about the mechanisms for transmission of substituent effects in terphenyls and similar molecules?

There have been several single parameter correlations of NMR data reported. Among these are simple Hammett correlations[2,10,11] of the type shown in eq 1, where δ is the

$$\delta = \rho\sigma + \delta_0 \tag{1}$$

chemical shift, σ is an appropriate classical reactivity (Hammett) parameter such as σ_I, σ_p, σ_p^+, σ_m, σ_R^-, σ_R^0, σ_R^+, σ_R^{BA}, or an NMR-derived constant such as θ,[16] ρ is a proportionality constant, and δ_0 is an adjustable constant. Most treatments[3,23] have applied the constraint that $\delta_0 = \delta_H$, the chemical shift of the unsubstituted parent compound, so that the single-parameter Hammett-type (H) equation is essentially eq 2, where $\Delta\delta = \delta - \delta_0$, the substituent-induced chemical shift.

$$\Delta\delta = \rho\sigma \tag{2}$$

For many chemical structures, a single-parameter relationship does not give valid correlations.[1,2,7-15] Hence, several dual substituent parameter (DSP) approaches have been used, among them the *F*,*R* scale of Swain and Lupton[24] and the σ_I,σ_R^0 scale of Taft.[25] The most generally useful of these is probably the Taft DSP equation (eq 3),

$$\Delta\delta = \rho_I\sigma_I + \rho_R\sigma_R \tag{3}$$

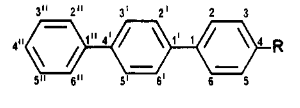
where σ_I is the Hammett inductive parameter and σ_R is one of the several Hammett resonance parameters.

Whether a dual-parameter scale is necessary or whether a single parameter scale will suffice to explain aromatic substituent effects has been the subject of much debate.[7,15,16,22] Reynolds and co-workers in a recent paper[15] have demonstrated that a DSP scale is significantly more precise in describing NMR substituent effects than one employing a single parameter. For more than 50 4-substituted styrene derivatives, they show that a DSP scale is both necessary and sufficient to account for the substituent-induced changes in the NMR parameters. The DSP approach has also been successfully used[21] in analysis of substituent electronic effects on the ^{13}C NMR spectra of 1- and 2-substituted azulenes, where good correlations between the DSP regression coefficients and CNDO-derived charge densities were obtained.

Bromilow and Brownlee[19] investigated in detail the use of the DSP equation and recommend that the comprehensive basis set[8,25] of substituents include at least two strong donors (NMe_2, NH_2, or OMe), two halogens (but not both Cl and Br), Me, H, one acceptor (NO_2, CN, or CF_3), and one carbonyl acceptor (COMe or COOR). This covers a wide range of substituent inductive and resonance properties. More recently, Bromilow and co-workers[17] have analyzed in great detail substituent effects on the ^{13}C NMR chemical shifts of 1,4-disubstituted benzenes. The nonadditivity of these effects was interpreted in terms of the local π-electron density at the para carbon. Through the use of calculated electronic charges and a DSP approach, the effects of a fixed substituent Y on the shifts of the para carbon with a variable substituent X were shown to be twofold: a sensitivity effect at X (essentially the shift-to-charge ratio) and an electron-demand effect exerted by Y, which either enhances or reduces the π-electron delocalization at X. These effects were accurately described by a modification of the DSP equation to include an electron-demand parameter, ϵ, for Y, which gives an effective resonance term in the resultant DSP–nonlinear regression or DSP-NLR equation (eq 4).

$$\Delta\delta = \rho_I\sigma_I + \rho_R\sigma_R/(1 - \epsilon\sigma_R) \tag{4}$$

In the present work, the substituent effects on the ^{13}C NMR chemical shifts of a series of 4-substituted *p*-terphenyls (**1**) were measured. The set of ten substituents



1, R = NO_2, $COOCH_3$, CN, H, CH_3, I, Br, Cl, NH_2, $N(CH_3)_2$

was more than adequate to constitute a minimum basis set[19] for DSP analysis. Correlations between the substituent-induced ^{13}C chemical shifts $\Delta\delta$ and the various σ values[8,23,26-29] were sought by using the single-parameter, DSP, and DSP-NLR equations (eq 2–4). Statistical tests[30] were used to determine the goodness of fit of the data at a given carbon to a given equation and set of parameters and to determine the best choice of an equation (model) if more than one good fit was obtained. For goodness of

---

(5) Happer, D. A. R.; McKerrow, S. M.; Wilkinson, A. L. *Aust. J. Chem.* **1977**, *30*, 1715.

(6) Ewing, D. F. In "Correlation Analysis in Chemistry: Recent Advances"; Chapman, N. B.; Shorter, J., Eds.; Plenum: New York, 1978; pp 357–396.

(7) Shorter, J. In "Correlation Analysis in Chemistry: Recent Advances"; Chapman, N. B.; Shorter, J., Eds.; Plenum: New York, 1978; pp 119–173.

(8) Wells, P. R.; Ehrenson, S.; Taft, R. W. *Prog. Phys. Org. Chem.* **1968**, *6*, 147.

(9) Charton, M. *Prog. Phys. Org. Chem.* **1968**, *6*, 175–268.

(10) Dewar, M. J. S.; Marchand, A. P. *J. Am. Chem. Soc.* **1966**, *88*, 3318.

(11) Schulman, E. M.; Christensen, K. A.; Grant, D. M.; Walling, C. *J. Org. Chem.* **1974**, *39*, 2686.

(12) Wilson, N. K.; Anderson, M. In "Mass Spectrometry and NMR Spectroscopy in Pesticide Chemistry"; Plenum: New York, 1974; pp 197–218.

(13) Wilson, N. K.; Zehr, R. D. *J. Org. Chem.* **1978**, *43*, 1768.

(14) Hugel, H. M.; Kelly, D. P.; Spear, R. J.; Bromilow, J.; Brownlee, R. T. C.; Craik, D. J. *Aust. J. Chem.* **1979**, *32*, 1511.

(15) Reynolds, W. F.; Dais, P.; MacIntyre, D. W. *J. Magn. Reson.* **1981**, *43*, 81.

(16) Edlund, U.; Wold, S. *J. Magn. Reson.* **1980**, *37*, 183.

(17) Bromilow, J.; Brownlee, R. T. C.; Craik, D. J.; Sadek, M.; Taft, R. W. *J. Org. Chem.* **1980**, *45*, 2429; Brownlee, R. T. C.; Sadek, M. *Aust. J. Chem.* **1981**, *34*, 1593.

(18) Nakai, Y.; Takabayashi, T.; Yamada, F. *Org. Magn. Reson.* **1980**, *13*, 94.

(19) Bromilow, J.; Brownlee, R. T. C. *J. Org. Chem.* **1979**, *44*, 1261.

(20) Adcock, W.; Cox, D. P. *J. Org. Chem.* **1979**, *44*, 3004.

(21) Holak, T. A.; Sadigh-Esfandiary, S.; Carter, F. R.; Sardella, D. J. *J. Org. Chem.* **1980**, *45*, 2400.

(22) Cornelis, A.; Lambert, S.; Laszlo, P.; Schaus, P. *J. Org. Chem.* **1981**, *46*, 2130.

(23) Brownlee, R. T. C.; Ehrenson, S.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.

(24) Swain, C. G.; Lupton, E. C., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4328.

(25) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 117–135.

(26) Katritzky, A. R.; Topsom, R. D. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 87.

(27) Hansch, C.; Leo, A.; Unger, S. H.; Kim, K. H.; Nikaitani, D.; Lien, E. J. *J. Med. Chem.* **1973**, *16*, 1207.

(28) Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley-Interscience: New York, 1975.

(29) Exner, O. In "Advances in Linear Free Energy Relationships"; Chapman, N. B., Shorter, J., Eds.; Plenum: London, 1972; p 37.

(30) Meyer, S. L. "Data Analysis for Scientists and Engineers"; Wiley: New York, 1975.

fit, χ^2 tests were used with the requirement that the confidence level be better than 95%. For the choice of model, *F* tests were used, again with the requirement of better than 95% confidence.

Experimental Section

Materials. Reagent grade or better *p*-terphenyl and 4-nitro-*p*-terphenyl were bought from Aldrich Chemical Co. The 4-bromo and 4-amino derivatives were bought from Alfred Bader Chemicals and the 4-chloro derivative from RFR, Inc. These were used as received. The remaining terphenyls and additional 4-amino-*p*-terphenyl were synthesized in these laboratories by the methods given below. All the terphenyls were checked for identity and purity by melting points, infrared spectroscopy, and gas chromatography–mass spectrometry and/or thin-layer chromatography.

4-Amino-1:1′,4′:1″-terphenyl. 4-Nitro-1:1′,4′:1″-terphenyl was hydrogenated (3 atm) at room temperature in *N*,*N*-dimethylformamide solution by using a 5% Pd/C catalyst. The solution was filtered, concentrated, and subjected to flash chromatography[31] over silica gel eluted with methylene chloride to give 4-amino-1:1′,4′:1″-terphenyl, mp 198–200 °C (lit.[32] mp 198 °C).

4-Iodo-1:1′,4′:1″-terphenyl. 4-Amino-1:1′,4′:4″-terphenyl (504 mg), dissolved in 20 mL of glacial acetic acid, was diazotized at room temperature by addition of 2 mL of a solution of 1.0 g sodium nitrite in 10 mL of concentrated sulfuric acid. The resulting diazonium salt was poured into a solution of 10 g of potassium iodide in 10 mL of water. The mixture was stirred for 0.5 h and then heated until gas evolution ceased. The mixture was cooled and filtered, and the solid residue was extracted with methylene chloride to give 682 mg of an orange solid, mp 230–242 °C. The solid was recrystallized from 1200 mL of 95% ethanol to yield 316 mg of 4-iodo-1:1′,4′:1″-terphenyl, mp 247–248.5 °C (lit.[33] mp 246–247 °C).

4-Methyl-1:1′,4′:1″-terphenyl. 4-Iodo-1:1′,4′:1″-terphenyl in anhydrous diethyl ether was treated with butyllithium, and the resulting salt was alkylated with dimethyl sulfate according to the procedure of Gilman and Weipert.[34] Removal of small amounts of *p*-terphenyl and final purification was accomplished by recycle chromatography with a Whatman Magnum 9 ODS 2 column and a mobile phase consisting of methanol/methylene chloride/water (80:10:10) to give 4-methyl-1:1′,4′:1″-terphenyl, mp 206–207 °C (lit.[34] mp 207–208 °C).

4-Cyano-1:1′,4′:1″-terphenyl. 4-Amino-1:1′,4′:1″-terphenyl (624 mg, 2.55 mmol) was suspended in 10 mL glacial acetic acid, and 2 mL of a solution of 1.0 g sodium nitrite in 10 mL concentrated sulfuric acid[35] was added at room temperature. There was an immediate reaction, and the suspension dissolved. The diazonium sulfate was precipitated by addition of 80 mL of anhydrous diethyl ether. The precipitate was filtered out on a Büchner funnel, washed with anhydrous ether, and dried on the filter paper. The dried salt[32] was added to a stirred solution of 2 g of copper sulfate pentahydrate and 3 g of potassium cyanide in 10 mL of water. When gas evolution slowed after approximately 15 min, the mixture was heated to complete the reaction. After cooling and the addition of 50 mL of water, the mixture was filtered. The resulting brown solid was extracted with hot acetonitrile. The organic solution was concentrated to dryness and subjected to successive flash chromatography[31] on silica gel. Elution with methylene chloride gave 353 mg of product, mp 193–197 °C. Rechromatography using toluene as the mobile phase gave 337 mg of yellow solid, mp 196–198 °C. Rechromatography using 75% toluene/25% hexane gave 255 mg of 4-cyano-1:1′,4′:1″-terphenyl as a pale yellow solid, mp 198–199 °C. Recrystallization from toluene gave material with the following: mp 198–199 °C [lit.[36] mp 186–188 °C (cyclohexane); lit.[37] mp 219–220 °C (alcohol)]; IR (KBr) 2230 cm^{-1}.

Anal. Calcd for $C_{19}H_{13}N$: C, 89.38; H, 5.13; N, 5.49. Found: C, 89.02; H, 5.38; N, 5.46.

4-(Carboxymethyl)-1:1′,4′:1″-terphenyl. 4-Cyano-1:1′,4′:1″-terphenyl (249 mg, 0.98 mmol) was dissolved in a mixture of 100 mL of methanol and 100 mL of anhydrous ether. This solution was cooled in an ice bath, saturated with anhydrous HCl, stoppered, and refrigerated for about 60 h. The solution was then added cautiously to 300 mL of water. The volume was reduced by half on a rotary evaporator, and the remainder was refluxed for 1.5 h. The cooled mixture was extracted several times with methylene chloride (total volume 500 mL). The organic layer was washed successively with water, saturated aqueous sodium bicarbonate, water, and saturated aqueous sodium chloride and was dried over anhydrous sodium sulfate. The organic solution was filtered and the solvent removed on a rotary evaporator to give 249 mg of crude ester, mp 221–223 °C. The crude product was sublimed at 150 °C (0.02 torr) and recrystallized twice from toluene to yield pure 4-(carboxymethyl)-1:1′,4′:1″-terphenyl as white needles: mp 223.5–224.5 °C (lit.[38] mp 228–230 °C); IR(KBr) 1720 cm^{-1}.

Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.09; H, 5.60.

4-(Dimethylamino)-1:1′,4′:1″-terphenyl. 4-Amino-1:1′,4′:1″-terphenyl (246 mg, 1.0 mmol) was dissolved in 25 mL of toluene by heating to about 50 °C and stirring, and 340 mg (1.0 mmol) tetrabutylammonium hydrogen sulfate and 5 mL 50% aqueous potassium hydroxide were added. Dimethyl sulfate was added in 100-μL increments. The course of the reaction was monitored by TLC (silica gel, methylene chloride) after each addition. Two products were formed. The reaction was not complete after addition of 1200 μL of dimethyl sulfate and was discontinued. The mixture was allowed to cool, 50 mL of water was added, and the layers were separated. The aqueous layer was washed with methylene chloride (2 × 50 mL). The organic extracts were combined, washed with water until neutral, washed with saturated aqueous sodium chloride, and dried over anhydrous sodium sulfate. The solution was filtered, and the solvent was removed on a rotary evaporator to yield 253 mg of a yellow solid. Sublimation at 170 °C (0.005 torr) afforded 175 mg of solid (mp 233–236 °C) containing two components, the dimethyl and the monomethyl products, by TLC (silica gel, 10% pyridine in hexane). This material was further purified by preparative liquid chromatography (Waters Associates Prep LC/System 500, one silica cartridge, mixtures of hexane/toluene containing 0.5% diethylamine) and recrystallized from hexane/toluene to yield 65 mg of 4-(dimethylamino)-1:1′,4′:1″-terphenyl as off-white leaflets: mp 237.5–239 °C; IR (KBr) 3031 (m), 2928 (m), 2900 (m), 2870 (m), 2796 (m), 1600 (vs), 1537 (m), 1510 (s), 1483 (s), 1445 (m), 1401 (m), 1350 (s), 1223 (s), 1167 (m), 1060 (m), 1005 (m), 950 (m), 842 (m), 812 (vs), 762 (vs), 728 (s), 690 (s), 660 (w) cm^{-1}; exact mass calcd for $C_{20}H_{19}N$ *m/e* 273.1517, found *m/e* 273.1517.

Spectra. Samples for NMR analysis were 0.500–2.18% (w/v) solutions in chloroform-*d* or methylene-d_2 chloride with a 0.5% Me_4Si internal reference. Both ^1H and ^{13}C NMR spectra were obtained with a Varian XL-100/Nicolet TT-100 Fourier transform NMR system with 12- or 18-mm probes. Carbon-13 spectral sweep widths of ±3 kHz with quadrature phase detection, flip angles of ~15°, pulse delays of 2–5 μs, and 16K Fourier transforms were employed. Proton broad-band decoupling was supplied by 100-Hz square-wave audio modulation of a single frequency centered on the proton aromatic resonances.

Assignments of the ^{13}C resonances were accomplished by standard techniques, employing single-frequency off-resonance and selective ^1H decoupling, measurements of ^1H–^{13}C spin–spin coupling constants, ^{13}C spin–lattice relaxation times,[1,39] and nuclear Overhauser enhancements.[13] Additional aid in assignments was provided by data for the 4-substituted[11] and 4,4′-disubstituted[12] biphenyls, with the assumption of additivity of substituent effects.

---

[31] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

[32] Pummerer, R.; Binapfl, J.; Bittner, K.; Schuegraf, K. *Chem. Ber.* **1922**, *55*, 3095.

[33] France, H.; Heilbron, I. M.; Hey, D. H. *J. Chem. Soc.* **1938**, 1364.

[34] Gilman, H.; Weipert, E. A. *J. Org. Chem.* **1957**, *22*, 446.

[35] Hodgson, H. H.; Mahadevan, A. P. *J. Chem. Soc.* **1947**, 325.

[36] Colonge, J.; Beundia, J.; Sabadie, J. *Bull. Soc. Chim. Fr.* **1967**, 4370.

[37] Brocklehurst, P.; Burawoy, A.; Thompson, A. R. *Tetrahedron* **1960**, *10*, 102.

[38] Demchak, R. J.; Fort, T., Jr. *J. Colloid Interface Sci.* **1974**, *46*, 191.

[39] Wilson, N. K., submitted for publication in *J. Magn. Reson.*

Table I. Carbon-13 NMR Chemical Shifts[a] of 4-Substituted *p*-Terphenyls

	Δδ, ppm											
substituent	C-1	C-2,6	C-3,5	C-4	C-1′	C-2′,6′	C-3′,5′	C-4′	C-1″	C-2″,6″	C-3″,5″	C-4″
NO_2	147.17	127.87	124.20	147.17	137.58	127.82	127.65	141.91	140.19	127.12	128.97	127.82
$COOCH_3$ [b]	145.41	128.00	130.46	129.62	139.24	127.29	128.00	141.39	140.81	127.38	129.29	128.08
CN	145.21	127.85	132.67	111.04	137.99	127.61	127.61	141.65	140.24	127.10	128.96	127.77
H	140.82	127.09	128.84	127.38	140.21	127.53	127.53	140.21	140.82	127.09	128.84	127.38
H[b]	141.00	127.33	129.23	127.82	140.47	127.82	127.82	140.47	141.00	127.33	129.23	127.82
CH_3	137.90	126.91	129.58	137.15	140.13	127.32	127.50	139.90	140.86	127.06	128.82	127.32
I	138.98	128.87	137.96	93.06	140.27	127.26	127.66	140.59	140.68	127.06	128.87	127.50
Br	138.92	128.64	131.97	121.65	139.69	127.64	127.50	140.60	140.60	127.06	128.87	127.32
Cl	139.34	128.40	128.86	133.35	138.81	127.40	127.52	140.53	140.59	127.05	128.80	127.35
NH_2	131.04	127.93	115.45	145.96	140.13	126.68	127.41	139.08	140.91	126.97	128.78	127.12
$N(CH_3)_2$	129.49	127.62	112.84	150.04	140.19	126.56	127.38	138.80	140.98	126.95	128.74	127.02

[a] In chloroform-*d* (10% w/v), except as noted. The precision is 0.31 Hz or 0.01 ppm. [b] In methylene-d_2 chloride.

Table II. Best Models for Transmission of Substituent Effects in 4-Substituted *p*-Terphenyls

							probabilities	
carbon	best model	best σ_R	ρ_I (std dev)	ρ_R (std dev)	ϵ (std dev)	λ[a]	fit, Pr > χ^2	model, Pr > *F*
1	DSP	$\sigma_R{}^0$	4.43 (1.70)	20.3 (2.43)		4.58	3.5×10^{-3}	3.1×10^{-2}
2,6	DSP	$\sigma_R{}^-$	2.60 (0.272)	−1.39 (0.341)		−0.535	1.5×10^{-3}	1.2×10^{-5}
1′	DSP-NLR	$\sigma_R{}^0$	−2.13 (0.568)	−1.65 (0.125)	5.29 (1.47)	0.775	4.7×10^{-3}	4.9×10^{-2}
2′,6′	H	$\sigma_R{}^0$		1.41 (0.364)			1.0×10^{-1}	4.0×10^{-2}
3′,5′	DSP	$\sigma_R{}^0$	0.159 (0.0493)	0.291 (0.0705)		1.83	5.4×10^{-2}	1.2×10^{-2}
4′	DSP-NLR	$\sigma_R{}^0$	2.03 (0.0212)	2.44 (0.0640)	−0.323 (0.0497)	1.20	1.0×10^{-10}	4.7×10^{-4}
1″	DSP	$\sigma_R{}^0$	−0.773 (0.0568)	−0.446 (0.0812)		0.577	1.2×10^{-4}	8.2×10^{-7}
2″,6″	H	$\sigma_R{}^0$		0.242 (0.0159)			2.7×10^{-5}	1.4×10^{-1}
3″,5″	DSP	$\sigma_R{}^0$	0.135 (0.0197)	0.207 (0.0282)		1.53	1.8×10^{-3}	1.3×10^{-4}
4″	DSP	$\sigma_R{}^0$	0.452 (0.0508)	0.767 (0.0726)		1.70	2.1×10^{-4}	2.0×10^{-5}

[a] Equal to ρ_R/ρ_I.

Exact mass measurements were made by manual peak matching at low resolution and by high-resolution runs on a Varian CH-5 mass spectrometer. Infrared spectra were obtained on a Perkin-Elmer 257 grating infrared spectrophotometer. Regression analyses and statistical parameters were obtained on an IBM 370 computer by using the SAS[40] general linear modeling (GLM) and the nonlinear regression (NLIN) with Gauss–Newton iteration procedures.

Results and Discussion

The ^{13}C NMR chemical shifts of the terphenyls in this study are given in Table I. The substituent effects, Δδ values, were obtained by subtraction of the chemical shifts of the unsubstituted compound from the corresponding chemical shifts of the substituted compound. The chemical shifts and Δδ values are similar to those reported for analogous carbons in benzene[41,42] and in biphenyl.[11,12,43] Although the transmission of substituent electronic effects in terphenyls shows the expected attenuation for carbons farther from the substituent, measurable changes in δ occur at all carbons, including small but real effects at the most remote carbon in the molecule, C-4″, 12 bonds removed from the substituent.

Correlations of Δδ values and σ parameters were sought by using eq 2–4. The σ values used were either the inductive parameters σ_I or the resonance parameters σ_R ($=\sigma_p$, $\sigma_p{}^+$, σ_m, $\sigma_m{}^+$, $\sigma_R{}^-$, $\sigma_R{}^0$, $\sigma_R{}^+$, or $\sigma_R{}^{BA}$) at each position. All of the appropriate σ_R parameters were tried in each equation at each position.

At positions 3–5, no statistically valid correlations were obtained between the σ parameters and the Δδ values. This lack of correlation at the ipso and ortho carbons is not surprising, since there are large differences in the potential steric or direct electric field effects from, for example, the nitro or dimethylamino groups or neighbor anisotropy effects from, for example, the bromine substituent.

At several positions, acceptable fits were obtained for more than one model and/or for several different σ_R parameters. For a given model, that set of σ_I and σ_R parameters was chosen that gave the best fit using the χ^2 test. If more than one model gave a good fit, the best model was chosen by using the *F* test of variances. The results are given in Table II. The probabilities given, Pr > χ^2 and Pr > *F*, are the probabilities that the values of χ^2 or *F* obtained could have arisen by random variations. Hence, the smaller Pr > χ^2 and Pr > *F*, the greater the confidence that can be assigned to the fit of a given model and to the choice of a given model over any others tried that also gave acceptable fits.

At only two positions (2′,6′ and 2″,6″) was a single parameter (H) relationship the best choice. At position 2′,6′ the fit was not particularly good, as evidenced by the large Pr > χ^2. Although the single-parameter fit was quite acceptable at position 2″,6″, the DSP fit was about as good. The large Pr > *F* at this position reflects the weakness of the choice between the H and DSP models for these carbons.

The DSP correlations were best at most of the remaining positions. However, the DSP-NLR correlations were better than the DSP correlations with probabilities greater than 0.951 and 0.999 53 at positions 1′ and 4′, respectively. In all these cases, both the inductive and resonance terms were important, as reflected in the values of the coefficients of these terms, ρ_I and ρ_R. Somewhat surprisingly, the

---

(40) Statistical Analysis System, SAS Institute, Inc., Raleigh, NC, 1979.

(41) Levy, G. C.; Nelson, G. L.; Cargioli, J. D. *Chem. Commun.* **1971**, *506*.

(42) Levy, G. C.; Nelson, G. L., "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972; p 81.

(43) Wilson, N. K. *J. Am. Chem. Soc.* **1975**, *97*, 3573.

relative importance of inductive electronic effects is substantial even in the distant ring. This is shown in the values of $\lambda = \rho_R/\rho_I$ for the carbons in this ring; even at C-4″, λ is only 1.70.

Since the response of the electronic system to the perturbation of the substituent is the common factor between NMR chemical shifts and σ values, changes in electronic charge densities at the particular carbons are important influences in these correlations. The nonlinearity of the $\Delta\delta$ vs. σ relationship at C-1′ and C-4′, both para-type positions in the central ring, may well reflect the decreased sensitivity of these carbons to substituent effects because of the moderation of the π-electron density changes at C-1′ and C-4′ by the terminal phenyl group. This effect is similar to the decreased sensitivity of the para carbon to mesomeric substituents observed by Bromilow and coworkers[17] in 1,4-disubstituted benzenes.

Since the ground and very low-lying excited states play a major role in determining ^{13}C NMR chemical shifts, the best σ_R parameter should be $\sigma_R{}^0$, which is more characteristic of the electronic ground state than, for example, $\sigma_p{}^+$. This is indeed the case for the resonance terms in the H, DSP, and DSP-NLR calculations, except at C-2,6. At C-2,6, the resonance and inductive effects have opposite signs, and $\sigma_R{}^-$ gives the best correlations.

The positive signs of the coefficients are as expected: electron-withdrawing substituents lead to decreased shielding of the molecule, and electron-releasing substituents lead to increased shielding. At C-1′ and C-1″, however, these signs are negative, indicating the resonance-modified redistribution of π-electron density that is especially effective along the long molecular axis.

An interesting aspect of the substituent effects in the terphenyls is that the transmission of these effects is quite similar to that in 4-substituted styrenes. The λ values obtained in this work for analogous positions are nearly identical with those calculated by Reynolds and co-workers.[15] The mean λ in this work is 1.46 with a 1.48 standard deviation, which is statistically indistinguishable from the mean λ in Reynolds' work of $\lambda = 1.48$ with a standard deviation of 1.82. Since the values of λ cannot be the same at all positions, the results rigorously support the necessity of a dual substituent scale.[15] The results also show that even for long-range effects of substituents on carbon chemical shifts, both inductive and resonance transmission of these effects are important in terphenyls.

Acknowledgment. We thank John T. Wilson, Steven T. Maher, Dolores James, and Ronald E. Block for valuable technical assistance and Victor Hasselblad for useful advice on statistics.

Registry No. 1 (R = NO_2), 10355-53-0; 1 (R = $COOCH_3$), 51166-76-8; 1 (R = CN), 17799-51-8; 1 (R = H), 92-94-4; 1 (R = CH_3), 28952-41-2; 1 (R = I), 1762-85-2; 1 (R = Br), 1762-84-1; 1 (R = Cl), 1762-83-0; 1 (R = NH_2), 7293-45-0; 1 (R = $N(CH_3)_2$), 80583-47-7.

Solvent Effect on the Kinetics of the Chlorine Isotopic Exchange Reaction between Chloride Ion and *O,O*-Diphenyl Phosphorochloridate or *O,O*-Diphenyl Phosphorochloridothioate

M. Mikołajczyk* and H. Slebocka-Tilk

Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Department of Organic Sulfur Compounds, 90-362 Lodz, Boczna 5, Poland

W. Reimschüssel*

Institute of Applied Radiation Chemistry, Technical University, 90-590 Lodz, Wroblewskiego 15, Poland

Received August 4, 1980

The effect of solvent on the kinetics of the chlorine isotopic exchange reaction between $^{36}Cl^-$ ions and *O,O*-diphenyl phosphorochloridate [$(PhO)_2POCl$, **1**] or *O,O*-diphenyl phosphorochloridothioate [$(PhO)_2PSCl$, **2**] has been investigated in nitromethane, acetonitrile, propylene carbonate, benzonitrile, nitrobenzene, and hexamethylphosphoric triamide. The rate constants decrease with increasing electrophilicity of the solvent. A good correlation between the logarithm of the rate constants and acceptor number (AN) of the solvent was obtained with identical slopes for reactions with phosphoryl and thiophosporyl compounds. The slopes for the dependences of $\Delta H^{\ddagger}$ or $T\Delta S^{\ddagger}$ vs. AN for chlorine isotopic exchange in **1** are opposite those for the exchange reaction in **2**, so a constant ratio of $k_{P=O}/k_{P=S}$ is observed, resulting from compensation of $\Delta H^{\ddagger}$ by $\Delta S^{\ddagger}$. The effect of solvent on the initial state (from solubility measurements) and the transition state of the reaction between $(PhO)_2PSCl$ and the Cl^- ion was evaluated. Changes of solvation of **2** have practically no effect on the kinetics of the reaction. Changes of solvation of the chloride ion and of the transition state primarily influence the rate constants and activation parameters of the investigated isotopic-exchange reaction.

Recently we found[1] that the reactivity decrease related to the substitution of oxygen by sulfur in the phosphoryl group of *O,O*-diaryl phosphorochloridates depends on the decrease of the positive charge on the phosphorus atom. This conclusion was based on the kinetic substituent effects of para-substituted benzene rings on the rate constants of the chlorine isotopic-exchange reaction between $(p\text{-}RC_6H_4O)_2POCl$ or $(p\text{-}RC_6H_4O)_2PSCl$ and chloride ion in acetonitrile. Good Hammett correlations of the rate constants with the Taft's σ^0 constants were obtained, and the values of the reaction constants ρ were found to be

---

[1] W. Reimschüssel, M. Mikołajczyk, H. Slebocka-Tilk, and M. Gajl, *Int. J. Chem. Kinet.*, 12, 979 (1980).

0022-3263/82/1947-1188$01.25/0